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A Search for New Bands in the Near Infra-red Spectra of CN, N_2^+, and BeF.

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Introduction.

Mulliken's paper "on a class of one-valence-electron emitters," [1] stimulated an attempt to search for new bands in the spectra of these molecules. The idea developed by Mulliken in this paper is that the total number of electrons in a di-atomic molecule may be distributed around the nuclei as follows. Each nucleus of the two separate atoms which combine to form the molecule, retains its K ring. Thus of the total number of electrons, four are retained in the two K rings of the two atoms. The successive rings which are supposed to encircle the whole molecule are assumed, on the octet theory, to be completed each by eight electrons. On this hypothesis, all diatomic molecules whose total number of electrons

[1] Phys. Rev., Vol. 26, p. 561, (1925).

is 13, *e.g.*, CN, N_2^+, BeF, CO^+ and BO, will have one complete ring of 8 electrons encircling the two K rings, but in addition possess one electron in the outermost ring. This electron is called the valence electron, and as all these molecules have a single electron in the outermost ring, they are classed as one-valence electron emitters. It is also implicitly assumed that it is this valence electron and this alone which is responsible for the emission of the various band systems of the molecule.

Many predictions follow from these assumptions. In the first place, there should be a striking similarity, not only in the nature of the electronic levels of all these molecules, but also in the structure of their bands and in the electronic transitions which give rise to them. Secondly, the electronic levels of all these molecules should be similar to those of the corresponding atom, which in this case is sodium having $(2+8+1)=11$, one outermost electron. Thus Mulliken was able to show that the successive electronic levels of all these molecules starting from the normal are 1^2S, 2^2P and 2^2S, identical with those of Na. He was also able to point out the striking similarity among the analogous bands of these molecules. Thus, *e.g.*, the violet cyanogen bands, the first negative Deslandres' bands due to CO^+, the β bands of BO, the first negative nitrogen bands, are all identical in their structure being due to the common transition $2^2S \rightarrow 1^2S$. Similarly, the red cyanogen bands, the low pressure or Comet-tail bands due to CO^+, the α bands of BO and possibly the ultra-violet BeF bands of Datta, are very probably identical in structure being all due to the transition $2^2P \rightarrow 1^2S$. In addition to these bands, there are the Baldet-Johnson combination bands and the BO combination bands, which are in all probability identical in structure, being due to the common transition $2^2S \rightarrow 2^2P$. It is clear that the similarity among the band systems of these molecules, appears to be very striking. The analogy to the corresponding atom, was also regarded as complete ;

but Jenkins[1] showed that the ^2P level of the α bands of BO is inverted, whereas the corresponding ^2P level in sodium is normal. It was assumed therefore, that the ^2P levels of all these other molecules are also inverted, and this discrepancy between the molecules and their corresponding atom continued till very recently, when Mulliken [2] explained the inverted nature of the level in terms of the new hypothesis about the structure of molecules to which we shall presently refer. The nature of the ^2P level in BeF however, is not yet certain, even theoretically. At the same time, it may be noted that many of the molecules are not known to emit certain band systems whose analogues are found to exist in the spectra of certain others. Thus taking the $2^2S \rightarrow 1^2S$ transition, band systems are known for this transition in all these molecules except BeF. The transition $2^2P \rightarrow 1^2S$, is known for all molecules except N_2^+. Lastly, the combination transition $2^2S \rightarrow 2^2P$, is unknown in the molecules CN, N_2^+ and BeF. It was thought that the bands due to these transitions in these molecules might be still undiscovered. Hence an attempt described in this paper was made, at a search for these undiscovered band systems.

Recent work of Hund and Mulliken.

It may well be pointed out at this stage that due to recent theoretical work of Hund,[3] and its extension and application to various molecules by Mulliken,[4] our ideas about the electron configurations in a molecule have undergone radical changes. The main features of the new idea, in so far as it relates to the electronic states of the molecule with which we are now

1 Proc. Nat., Acad. Sc., Vol. 13, p. 496, (1927).
2 Phys. Rev., Vol. 32, p. 221, (1921).
3 Papers in Zeit. f. Physik, 1926, 1927.
4 Phys. Rev., Vol. 32, pp. 186-222, (1928) ; also pp. 761-772.

concerned, may be stated as follows. A diatomic molecule may be regarded as an interpolation between the two limiting cases, (1) two separate constituent atoms, (2) the united atom formed by the hypothetical process of fusing together the nuclei of the two atoms. The work necessary to separate the nucleus of the united atom into the two nuclei which exist in the molecule, manifests itself as a strong, axially symmetrical though not uniform electrical field in the molecule. Under the influence of this field, the electronic configurations of the separate atoms undergo changes, which can be determined for each atom separately by studying how the quantum numbers l and s of the atoms behave in a strong electrical field. Thus to take the classical example of a boron atom in a ^2P state having $l=1$ and $s=\frac{1}{2}$, we find that in a strong electric field it splits up into six components, the so-called strong field components which can be avoided from falling together in pairs by imagining a temporary magnetic field parallel to the electric axis, as follows.

σl	0	0	+1	+1	−1	−1
σs	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$

Similarly, a ^3P oxygen atom having $l=1$, $s=1$, will give rise to the following nine strong field components :—

σl	0	0	0	+1	+1	+1	−1	−1	−1
σs	0	+1	−1	0	+1	−1	0	+1	−1

The molecular combination of these two atoms, *i.e.*, a ^2P boron atom and a ^3P oxygen atom, will give rise to the following 54 ($=6\times9$) strong field components, on Hund's principle that in the process of this union "no state is lost."

	$\sigma l=$	0	0	0	0	+1	+1	+1	+1	−1	−1	−1	−1	
	$\sigma s=$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+1\frac{1}{2}$	$-1\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+1\frac{1}{2}$	$-1\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+1\frac{1}{2}$	$-1\frac{1}{2}$	
states	54=	6	6	3	3	4	4	2	2	4	4	2	2	
		+2	+2	+2	+2	−2	−2	−2	−2					
		$+\frac{1}{2}$	$-\frac{1}{2}$	$+1\frac{1}{2}$	$-1\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+1\frac{1}{2}$	$-1\frac{1}{2}$					
		2	2	1	1	2	2	1	1					

These 54 states give rise to the following molecular states on withdrawal of the imagined magnetic field. Of the 18 states having $\sigma l=0$, 12 can be arranged so as to give *three* $^4\Sigma$ states having $\sigma l=0$, $\sigma s=1\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -1\frac{1}{2}$, and six to give *three* $^2\Sigma$ states having $\sigma l=0$ and $\sigma s=\frac{1}{2}, -\frac{1}{2}$. Of the 24 states having $\sigma l=+1, -1$, eight give rise to *two* $^2\Pi$ states having $\sigma l=+1, -1, \sigma s=+\frac{1}{2}, -\frac{1}{2}$, and 16 give rise to *two* $^4\Pi$ states having $\sigma l=+1, -1, \sigma s=1\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -1\frac{1}{2}$. Similarly the 12 states having $\sigma l=+2, -2$, can be arranged so that four of them give rise to *one* $^2\Delta$ state having $\sigma l=+2, -2$, $\sigma s=\frac{1}{2}, -\frac{1}{2}$, and eight of them to *one* $^4\Delta$ state having $\sigma l=+2, -2$, and $\sigma s=1\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -1\frac{1}{2}$. It will be noted that capital Σ, Π or Δ letters, in the case of molecules, the σl values rather than l values as in the case of atomic spectra.

Thus it will be seen that when we place an atom in a strong electric field, as in a molecule, the electronic shells undergo radical changes. In an atom we know that the electrons are grouped as follows :—

Orbits	1_1 (S)	2_1 (S)	2_2 (P)	3_1 (S)	3_2 (P)	3_3 (D)
Electrons	2	2	6	2	6	10

that is to say, an S shell having $l=0$, is completed by two, a P shell by six and a D shell by ten electrons. Under the

influence of an electric field the l values are broken up, giving $\sigma l = 1, 0, -1$, in the P shell and $\sigma l = 2, 1, 0, -1, -2$ in the D shell. Thus the P shell will be split up into an S shell of two electrons having $\sigma l = 0$ and a P shell of four electrons having $\sigma l = \pm 1$. The two former can then be designated as S^P electrons and the four latter as P^P electrons, the main letter indicating σl and the superscript l. Similarly the ten electrons of the D shell split up into two S^D, four P^D and four D^D electrons. Thus whereas in atoms one could write down the electron states as, $(1S)^2$, $(2S)^2$ $(2P)^6$, in molecules we should write $(1S^S)^2$ $(2S^S)^2$, $(2S^P)^2$ $(2P^P)^4$.

This may be made clearer by taking an example say the boron atom considered above. The electronic configuration of a boron atom is $(1S)^2$, $(2S)^2$ $(2P)^1$. The two S shells being complete, it is only the one electron in the P shell which is responsible for the electronic state of the normal atom, which will therefore be ^2P having $l = 1$, $s = \frac{1}{2}$. In a strong electric field or in a molecule the configuration will be either

$$(1S^S)^2,\ (2S^S)^2\ (2S^P)^1 \text{ with } \sigma l = 0 \text{ and } \sigma s = \pm\tfrac{1}{2} \quad \ldots\ (1)$$

or

$$(1S^S)^2,\ (2S^S)^2\ (2P^P)^1 \text{ with } \sigma l = \pm 1 \text{ and } \sigma s = \pm\tfrac{1}{2} \ldots\ (2)$$

Similarly, the electron configuration of an oxygen atom being $(1S)^2, (2S)^2\,(2P)^4$, it gives rise in the normal state to three electronic states ^3P, ^1D, ^1S. Each of these states produces a number of different electronic configurations in a molecule. These in combination with (1) and (2) give rise to a number of molecular states. Thus the ^3P state in the atom gives rise to the following configurations :—

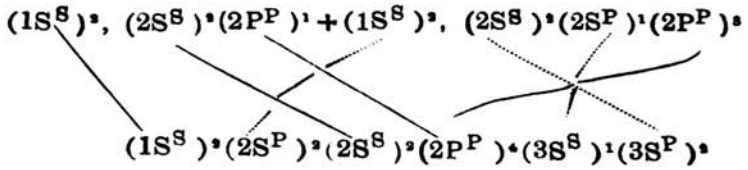
$$(1S^S)^2,\ (2^S)^2\ (2S^P)^2\ \ (2P^P)^2 \quad \ldots\ (3)$$

and

$$(1S^S)^2,\ (2S^S)^2\ (2S^P)^1\ (2P^P)^3 \quad \ldots\ (4)$$

By combining any one of the configurations (1) or (2) with any other of the configurations (3) or (4), we can obtain a

number of electronic states for the BO molecule. To take an example, combining (2) with (4) we get,



as the molecular configuration. Many things are worthy of attention here. On combination some of the strong field electrons retain all their quantum numbers in tact, while some have to undergo radical changes in most of their quantum numbers, in satisfaction of the Pauli principle. Those which have undergone such changes are denoted by dotted lines. It will be observed that all of these promoted electrons as they are called, have their principal quantum numbers increased by unity. It is not definitely known whether when such promotion takes place, the l value of the electron, denoted by the superscript letter undergoes changes. Mulliken inclines to the view that except in the case of the simplest molecules like H_2^+ where l increases with the principal quantum number, l usually undergoes changes of $0, \pm 1$. The resultant electronic configuration of the molecule has all its shells complete except the $(3S^S)$ shell. This contains one electron and the molecular state therefore is determined by this electron. It is clear that in this case it will be a $^2S^S$ state having $l=0$, $\sigma R=0$ and $\sigma s=\frac{1}{2}$.

Similarly, one can obtain all possible molecular states of the BO molecule by combining (1) or (2) with any of the various strong field configurations which can be similarly deduced, of an oxygen atom in the ^1D and ^1S states.

It is clear that the number of possible electronic states for a molecule even taking two atoms in their normal states is very large. Many of these states are not realised in practice. What are the selection principles, which render some

of these as improbable and the rest as probable, is not yet clear. However, there is the Hund's rule, that σl and s for the molecular state should be obtainable from the atomic σl and S values by addition, or in other words, atoms into which a molecule in a given state can dissociate must be in states which have l and s values compatible with σl and s values of the molecule. Mulliken[1] has shown that this rule is invariably obeyed with two possible exceptions—one state of N_2 and one state of O_2. Another factor which appears to govern such selection may be called the rule of least promotion. Molecular states involving as few promotions of the electrons of the constituent atoms as possible appear to be more stable from energy considerations and therefore more probable.

Some important conclusions from this hypothesis of molecular formation are: first, the transitions occurring in molecules are not always of the optical type, but very often belong to the X-ray type. In other words, it is not always the electron or electrons in the outermost shell that are capable of radiation. On the contrary it is almost always the electrons in an inner incomplete shell that give rise to molecular radiations. Secondly, levels of the same type, S, P or D etc., usually differ from one another according to the l value which is denoted by the superscript. Thus among S levels, we may have S^S, S^P, S^D, etc., levels which though identical in σl values, are essentially different from one another in having differing l values. Similarly among P and D levels we get P^P, P^D, etc., and D^D, D^F, etc., levels. This explains why in molecules, we usually meet with transitions between similar levels *e.g.*, S→S, P→P. The main letters do not signify as in atomic spectra l values but denote σl values and $\Delta\sigma l$. O is not only not forbidden but appears

[1] Phys. Rev., Vol. 32, p. 772, (1928).

to be one of the frequent transitions. On the other hand, transitions like say, $S^S \rightarrow S^S$ or $P^P \rightarrow P^P$ or $S^P \rightarrow P^P$, are forbidden for symmetrical molecules[1] since they involve $\Delta l = 0$; for other molecules such transitions are weak. Thus whenever a strong transition between levels having identical σl values occurs, it appears to be significant of the fact that the l values of the levels differ by unity. The $^2S \rightarrow {}^2S$ transition observed in the case of all the molecules considered in this paper, must therefore evidently be either $^2S^S \longleftrightarrow {}^2S^P$ or $^2S^P \longleftrightarrow {}^2S^D$. It also seems likely that a transition involving $\Delta l > 1$, *e.g.*, $S^S \longleftrightarrow S^D$ is forbidden. This has an important bearing on the existence or otherwise of the transitions which we seek to discover in these experiments, and we shall revert to it later after presenting experimental results.

Experimental.

(*a*) *The Cyanogen Spectra.*

Two band systems attributed to CN are known,[2] both of which have the same final electronic state. One in the ultra-violet known as the violet CN system is degraded towards the violet and the electronic transition giving rise to it is known to be $^2S \rightarrow {}^2S$. The other lies in the infra-red and visible portions of the spectrum. This is known as the red CN system degraded towards the red, the transition being $^2P \rightarrow {}^2S$. The purpose of these experiments was to search for the hypothetical band $^2S \rightarrow {}^2P$.

As is well-known, the wave numbers of the origins of the bands forming a system are usually expressed by the following formula :—

$$\nu = \nu_0 + (\omega_0' n' - \omega_0' x' n'^2) - (\omega_0'' n'' - \omega_0'' x'' n''^2).$$

[1] *Cf.* Mulliken, *loc. cit.*, p. 202.

[2] Report on Molecular Spectra, p. 230.

where, ω_o' and ω_o'' are frequencies of vibration of the molecule for infinitesimal amplitudes, and ν_o the origin of the band system which is identical with the origin of the vibrationless band, the so-called 0-0 band. Unless fine structure analysis is done, we shall have no knowledge of the positions of the origins of the bands; but it is observed that the distance between the origin of the band and its head, which is the one offering easy measurement, may be assumed to be fairly constant, so that the same equation is usually adopted to represent the heads of the band system. $(\omega_o'n' - \omega_o'x'n'^2)$ is also often described as the initial vibrational function and $(\omega''_o n'' - \omega''_o x''n''^2)$ as the final vibrational function. According to theory, the direction of degradation of the bands depends, on the relative values of the moments of inertia of the molecule, in the initial state (I') and in the final state (I''). Thus if I' > I'', the bands degrade to the red and *vice versa*. The frequency of vibration ω_o is inversely proportional to I and thus if $\omega_o'' > \omega_o'$, the band degrades to red and if $\omega_o'' < \omega_o'$ it degrades to the violet.

The equations representing the violet and red CN systems are :—

$$\text{Violet CN}: \quad \nu = 25797{\cdot}8 + (2143{\cdot}9n' - 20{\cdot}25n'^2) - (2055{\cdot}64n'' - 13{\cdot}75n''^2).$$

$$\text{Red CN}: \quad \nu = \left.\begin{matrix} 14430 \\ 14374 \end{matrix}\right\} + (1728{\cdot}5n' - 13{\cdot}5n'^2) - (2055{\cdot}64n'' - 13{\cdot}75n''^2).$$

The hypothetical combination system $^2S \rightarrow {}^2P$, should then be represented by,

$$\left.\begin{matrix} \nu = 11367{\cdot}8 \\ 11311{\cdot}8 \end{matrix}\right\} + (2143{\cdot}9n' - 20{\cdot}25n'^2) - (1728{\cdot}5n'' - 13{\cdot}5n''^2).$$

and be degraded towards the violet since $\omega_o' > \omega_o''$. The origin of the band thus lies at about 8797 λ and the system therefore could be photographed on a neocyanine plate. But measurements of the red CN band system described below indicate that the origin of the red CN system is not at 14430 ν, which is at least a (2-0) band, but further up on the longer wavelength side. This shift in the origin affects the origin of the combination bands and assuming the red CN band observed at 10938 ν (see below) as the 0-0 band, it is clear that the combination system will, if existing, be in the visible at about 14860 $\nu = 6727{\cdot}5$ λ.

The spectra of cyanogen were produced by the action of active nitrogen on chloroform, the method adopted being similar to the one described by Strutt.[1] The chloroform was contained in a side bulb and its flow was regulated by a needle valve. As we were not interested in the violet CN bands only the red CN bands were photographed on the glass c. d. spectrograph described in the next paper. Neocyanine plates hypersensitised by ammonia before use were employed to photograph the near infra-red spectrum and panchromatic plates for the visible spectrum. The neocyanine plates recorded a number of bands degraded to the red. The panchromatic plates recorded the known red CN bands interspersed with some bands degraded to the violet which appeared like the combination bands we were searching for, but which later, were identified as the first positive nitrogen bands. Except these there were no new bands registered on the plates and hence it is concluded that the combination bands are absent. Measurements of the red CN bands were made on four independent plates and the mean value of

[1] Bakerian Lecture, Roy. Soc. Proc., Vol. 85A, p, 219, (1911) and later papers.

the wave-numbers of the band heads were arranged as follows :—

$\frac{n''}{n'}$	0.	1.	2.	3.	4.	5.	6.
0	... ... 10938·0*	...	...	...	...	...	...
1	12637·6 664·1 697·4*	...	...	...	—	...	...
2	14368·6 395·9 × 433·1	12331·8 356·1 392·5*	...	...	...	...	...
3	16087·2 107·2 142·8	14043·1 065·4 099·4	12023·8 048·4 086·0*	...	...	...	...
4	...	15731·1 750·7 787·8	13714·4 737·5 769·3	11726·5 750·3 782·4*	...	...	...
5	...	...	15371·6 393·3 430·4	13380·6 407·1 439·2	... ... 11480·4*	...	...
6	...	...	17007·6 024·7 068·9	15017·7 037·5 074·5	13051·9 077·5 106·5	...	...
7	...	...	18614·3 631·5 671·3	16626·4 644·7 681·1	14661·6 681·9 715·8	12716·5 748·6 782·0	...
8	...	...	...	18209·6 224·8 262·8	16245·1 263·6 300·9	14306·7 327·9 362·2	...
9	...	...	...	...	17803·6 818·2 856·3	15865·4 880·8 919·0	...
10	...	⋮	...	...	—	17394·3 410·0 448·0	15479·9 502·6 542·1

The bands show three heads under low dispersion, the fourth head being masked by structure lines. There is no doubt, however, that the transition is $^2P \longrightarrow {}^2S$, as the unpublished work on the fine structure analysis, by Mulliken and Roots, is reported to show.[1] There should thus be two R, two P and

[1] Phys. Rev., Vol. 32, p. 186, 222, (1928).

two Q type branches of which R and Q branches go to form heads. The bands marked* are extensions of the red CN system. The band marked × is the 0-0 band as hitherto accepted. But it is clear that it is not the true 0-0 band of the system. Assuming the band at 10938ν to be the 0-0 band, a justification for which assumption will be given later, we get the following vibrational equation deduced from the present data:

$$\nu \text{ head} = 10938 + (1782n' - 13{\cdot}5n'^2) - (2055n'' - 13{\cdot}28n''^2)$$

This does not completely invalidate the existing analysis of the red CN system. The final vibrational function remains of course, the same, as also does $\omega_0'x'$; but the origin of the system is changed and the value of ω_0' also changes. This will have an effect on the value of the energy of dissociation D^v, of the initial level ^2P of these bands. If we assume with Mulliken, $D^v = \frac{\omega_0'}{4\omega_0x'}$, cm^{-1}, we can calculate D^v for the level in cm^{-1} and convert it into volts (8085 cm^{-1} = 1 volt). Mulliken [1] has calculated D^v according to old values of ω_0' and $\omega_0'x'$ and its value then is 6·8 volts. According to the present results its value is 7·3 volts. The total energy of dissociation D which is obtained by adding the electronic energy of the level, will be 7·3+1·3=8·6 volts, the same as that calculated on the old values. Of course, if the band at 10938ν is not the 0-0 band of the system, the value of D^v will increase but so also will D increase; for supposing 10938ν is the 1-0 band, it can be shown that D^v will be 7·5 and D will be 9·1 volts. This appears to be improbable on other considerations, as will be shown later and therefore, it appears certain that the band at 10938ν is the real 0-0 band of the system.

(b) N^+_2.

As remarked previously, only one band system is known for this molecule, which is due to the transition $^2\Sigma \longrightarrow {}^2\Sigma$. Besides these two levels, a third at about 24 volts has been

[1] *loc. cit.*, p. 266.

found by Hogness and Lunn [1] in their positive ray experiments. This has also been designated as ^2S, but no band system is yet known, which involves this level. We seek to locate the ^2P level and discover the bands due to the transitions, $^2S \longrightarrow {}^2P$ and $^2P \longrightarrow {}^2S$. Unlike in CN, we cannot say in what region of the spectrum these hypothetical bands might lie. If we assume however, that the ^2P level is at about 12500ν, this would also be the origin of band $^2P \longrightarrow {}^2S$, while the band $^2S \longrightarrow {}^2P$ will have as its origin about 13000ν. Any other value much lower or higher than this would throw one of these well into the visible and it is very unlikely that such a band in the visible, has escaped the notice of the numerous workers on the negative nitrogen bands. It was thought therefore best to investigate the infra-red region accessible to the neocyanine plates.

Negative nitrogen bands occur in the cathode glow of discharge tubes containing nitrogen but they are better developed by a mild condensed discharge in high pressure helium with a trace of nitrogen. [2] High frequency discharge under these circumstances improves the intensity of the bands of higher wavelengths. [2] The method adopted in these experiments was entirely different. The following diagram shows the apparatus used :—

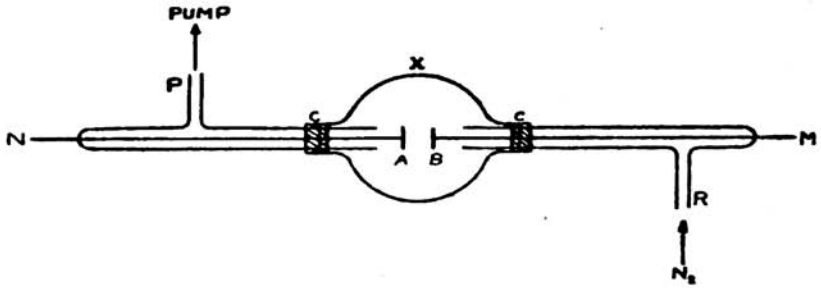


FIG 1

X is a glass vessel (spherical) about 6″ in diameter. AN,

[1] Phys. Rev., Vol. 26, p. 786, (1925). [2] Phil. Mag. Vol. 50, p. 195, (1925).

BM are two long stout nickel electrodes having discs at A and B at a distance apart of 1·5 *cm.* The electrodes are held in position by corks in glass tubes which are pushed into X through rubber corks at C,C. R is a tap opening to the reservoir of nitrogen while P goes to the pump. The apparatus was sealed gas-tight by sealing wax. After exhausting the apparatus a quantity of nitrogen sufficient to maintain a discharge obtained from a direct current generator, delivering 600 volts, was introduced. Under these conditions, the whole of the bulb was filled with a brilliant glow showing the negative bands strongly, the positive column being reduced to a speck on the positive electrode. Photographs taken with sufficiently long exposures, about 15 to 20 hours recorded no new bands.

(*c*) *Beryllium Fluoride.*

As in N_2^+, only two levels are known for this molecule; the transition between these two levels gives rise to the ultra-violet BeF bands, which were measured under high dispersion by Datta.[1] An interpretation of these bands was first given by Mulliken [2] and recently by Jevons, [3] both of whom made a vibrational analysis of the system. The presence of Q heads in these bands is taken to be an indication of the transition $^2P \rightarrow {}^2S$. We have therefore to locate the upper ^2S level and discover the bands $^2S \rightarrow {}^2S$ and $^2S \rightarrow {}^2P$. Jevons[3] has also recorded some new bands; but since they show no relation to the known band system, their origin is uncertain. Jevons thinks that they are possibly due to a BeO or BeF_2 molecule.

The production of the BeF bands is very simple. Potassium beryllium fluoride in carbon arc develops these bands very strongly. This procedure was therefore adopted and photographs were taken both in the ultra-violet and in the

[1] Phys. Rev., Vol. 26, p. 561, (1925).
[2] Roy Soc. Proc., Vol. 122A, p. 211, (1929).
[3] Roy. Soc. Proc., Vol. 101A, p. 187, (1922).

near infra-red. Some bands were recorded in the ultra-violet at about 1900λ ; but they were found to be due to CaF as an impurity in the salt used. Excepting these no new bands were recorded in the visible or the ultra-violet region. In the near infra-red however, some bands were recorded, which could not be measured on account of the very close packing of the band heads due to want of sufficient dispersion in the spectrograph used. It is hoped to photograph these bands under higher dispersion when opportunity offers.

Discussion.

Leaving aside BeF for which further experimental work is necessary, we may try to account for the absence of other band systems which we sought to discover. The molecules CN, N_2^+, CO^+ and BO were till recently classified as analogous and Mulliken[1] suggested the following molecular electronic configurations for the three levels of these molecules :—

Lower ^2S, $(A)^6, (mS^P)^2 (2P^P)^4 (nS^X)^1$;
^2P, $(A)^6, (2P^P)^3 (nS^X)^2$;
Higher ^2S, $(A), (mS^P)^1 (2P^P)^4 (nS^X)^2$.

Here A denotes the undetermined closed shell configuration of the six most firmly held electrons, m and n are undetermined principal quantum numbers, and X is S or D. Thus the lowest level is either $^2S^S$ or $^2S^D$, the ^2P level is either $^2P^P$ or $^2P^D$ and the uppermost level is $^2S^P$. All the three levels of BO can be formed from normal atoms B and O; similarly the levels of CO^+ from either normal C^+ and O or normal C and O^+. But in the case of CN and N_2^+ as Mulliken[2] has shown, normal C(or N^+) and normal N yield only one ^2S state and one ^2P state. The other ^2S state must then involve at least one excited atom. That this ^2S state which involves an excited atom, is the normal state of CN and N_2^+,

[1] *loc. cit.*, p. 204.
[2] Phys. Rev., Vol. 32, p. 765, (1928).

is evident from the peculiar reversal of energy order in the levels of both of these molecules. Thus for N_2^+ Herzberg's[1] work shows that the total energy D required to excite the molecule and dissociate it, is,

for lower ^2S, 26 volts ; for higher ^2S, 24 volts.

These values of D for the two states can only be explained as Mulliken shows, on the hypothesis that the higher ^2S state is given by normal N^+ and N, and the lower ^2S by N^+ and an excited N (N′) atom. It can be shown that a similar hypothesis is necessary to explain the observed D values of the states of the CN molecule. Recent work of Jenkins[2] on violet CN bands shows that the D value for the upper ^2S state of CN is < 9·9, the present value based on earlier work on the violet CN bands. On the assumption that the lower ^2S level of CN if built up of normal C and N atoms and the upper ^2S level of C and N′ (in a ^2P or ^2D state), one gets for the D value of the upper S state $9·5+1·15$ or $+2·40=10·7$ or 11·9 according as N′ is in a ^2P or ^2D state. This value of D is much greater than 9·9 which is itself shown by Jenkins' experiments to be much greater than the real D value. On the other hand, if we assume that the upper level is built up from normal C and N atoms, taking D=8·4 for this level as a probable value from Jenkins' experiments, we obtain for the lower ^2S level built from C and N′ (in a ^2P state), $D=8·4+1·15=9·55$ the observed value. The D value for the ^2P state is 8·6 in agreement with the hypothesis that this state is derived from normal atoms. Incidentally, this shows that it is very likely that the band at 10938ν of the red CN system observed in these experiments and labelled as the 0-0 band is the real 0-0 band. For otherwise as shown previously, the D value for this level will be = or > 9·1 volts, and it would require to be built up from at least one excited atom, which is not the case.

[1] Ann. der Phys., Vol. 86, p. 206, (1928). [2] *Cf.* Mulliken, *loc. cit.*, p. 765.

Conclusion.

In view of these facts, it is necessary to distinguish between the molecular levels of CO^+ and BO on the one hand and those of N_2^+ and CN on the other. The levels of the two former molecules are all built up from normal atoms and it seems fairly certain that the following representation of the levels is correct :—

Upper ^2S : $^2S^P$
^2P: $^2P^P$
Lower ^2S : $^2S^S$

This explains the existence of the two strong transitions $^2S^P \rightarrow {}^2S^S$ and $^2P^P \rightarrow {}^2S^S$, involving $\Delta l = 1$ and the weak transition $^2S^P \rightarrow {}^2P^P$, which in symmetrical molecules is completely forbidden. For CN and N_2^+, the following appears to be the correct designation :—

Upper ^2S : $^2S^S$
^2P : $^2P^D$
Lower ^2S : $^2S^P$

This explains the two strong transitions $^2S^S \rightarrow {}^2S^P$ and $^2P^D \rightarrow {}^2S^P$ in CN ; the absence of the transition $^2S^S \rightarrow {}^2P^D$ can be explained on the plausible assumption that $\Delta l > 1$ is forbidden. In N_2^+, the transition $^2P^D \rightarrow {}^2S^P$ is also not observed but it is very likely as Mulliken thinks, that this system lies in the infra-red beyond the range of the available photographic plates. In the case of N_2^+ one of the transitions $^2S^S \rightarrow {}^2P^D$ or $^2P^D \rightarrow {}^2S^P$ is further ruled out on Hund's hypothesis that for symmetrical molecules, out of three transitions possible among three given levels, only two should occur.

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